



Proposed mechanisms for the removal of nitrate from water by platinum catalysts supported on polyaniline and polypyrrole

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ABSTRACT

Platinum nanoparticles have been synthesized on polyaniline (PANI) and polypyrrole (PPy) as supports using H_2PtCl_6 as metal precursor and a reducing treatment with cold Ar plasma. The catalytic activity of the polymer-supported catalysts in the reduction of aqueous nitrate with H_2 at room temperature was evaluated. These systems are able to considerably decrease the concentration of nitrate in water in only 5 min. The mechanism of the nitrate abatement process is determined by the nature of the conducting polymer. The nitrogen functionalities in polyaniline are external to the ring system, and favor nitrate retention at the platinum complex either by the formation of an adduct or by nitrate participating as a ligand. In contrast, polypyrrole possesses aromatic nitrogen atoms with a considerably more important steric hindrance. In this case, ion exchange between the counter ions in the doped polymer (SO_4^{2-}) and nitrate from water is produced, followed by reduction of nitrate by hydrogen chemisorbed on the platinum nanoparticles.

1. Introduction

Since the discovery of electrical conducting properties of conjugated polymers (as polypyrrole and polyaniline) promoted by doping, they have been studied for a great variety of applications such as lightweight battery electrodes, electromagnetic shielding devices, anticorrosion coatings, etc. The main issue that is useful for most applications is not the metal-like electrical conductivity itself, but the combination of electrical conductivity and polymeric properties such as flexibility, low density and ease of structural modification that suffice for many commercial applications [1]. However, their use in catalysis has not been extensively studied.

Among conducting polymers, polypyrrole (PPy) and polyaniline (PANI) have attracted great attention. Their hetero-aromatic and extended π -conjugated backbone structure provide them with chemical stability and electrical conductivity, respectively. However, the π -conjugated structure is not enough to produce appreciable conductivity on its own; a doping process, which can be achieved chemically or electrochemically, is necessary. This produces a partial charge extraction from the polymer chain and, depending on the doping degree,

polypyrrole and polyaniline can exhibit multiple inherent oxidation states. Charge carriers are located in the main chain and compensated by counter-ions.

The process of chemical oxidative polymerization of PPy and PANI is usually followed by visible changes in the color of the polymerization solution. PPy appears yellow-green and dark blue-gray in its neutral (non-conducting) and oxidized (conducting) forms, respectively. When the pyrrole monomer is put into contact with an oxidant (Scheme 1), an initially colorless solution turns blue and dark blue after a while, indicating the formation of oligomers. Some time later, the precipitation of a dark blue or black solid polymer is observed, thus corresponding to the conducting PPy [2]. On the other hand, PANI shows the greatest number of characterized forms among the conducting polymers [3]. The polymer is composed of reduced (B-NH-B-NH) and oxidized (B-N=Q=N-B) units where B and Q are benzenoid and quinoid rings, respectively. The variation of the amine and imine ratio in its structure gives rise to several forms: leucoemeraldine, which contains only benzenoid rings and is the completely reduced form, emeraldine containing half benzenoid rings and half quinoids and pernigraniline that only shows quinoid rings. In turn, each of these forms can be found

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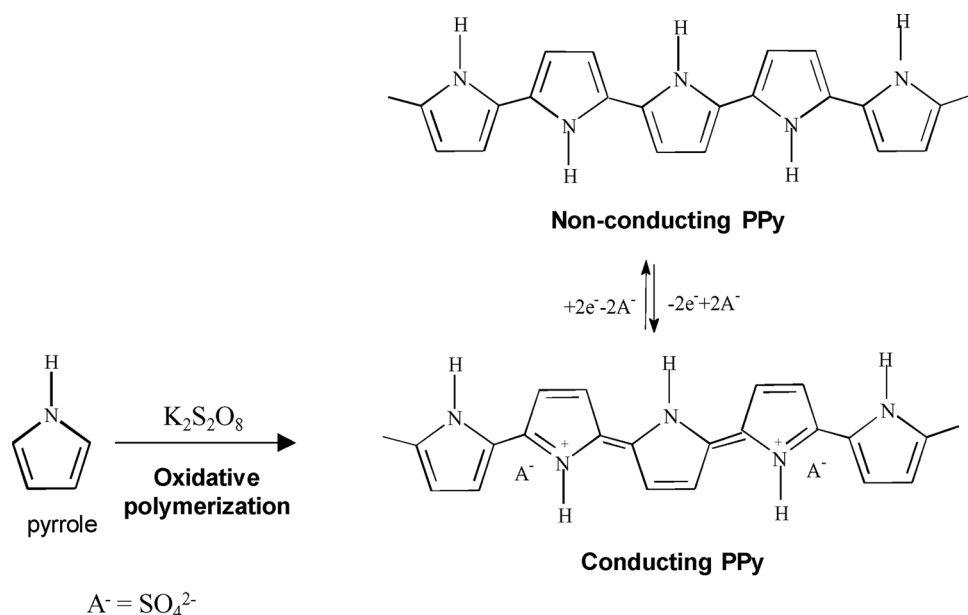
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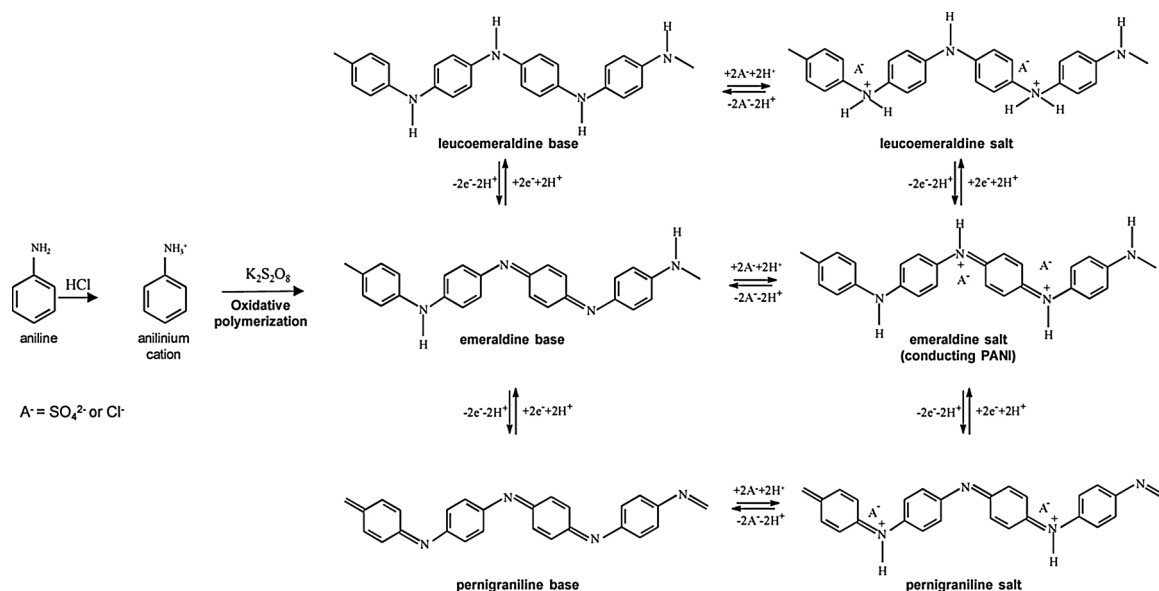
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Scheme 1. Scheme showing the oxidative polymerization of pyrrole with potassium peroxydisulfate producing conducting PPy.



Scheme 2. Scheme showing the oxidative polymerization of aniline with potassium peroxydisulfate in acidic aqueous medium producing conducting PANI.

protonated or deprotonated, producing a total of six forms, which can be transformed into one another by reactions of oxidation, reduction, protonation and deprotonation. Scheme 2 shows the different reactions that take place between the different states of PANI. Protonated forms of PANI are known by the term “salt”, while non-protonated forms are called “base”. They show different colors depending on their oxidation state and their protonation. The leucoemeraldine base is clear yellow, emeraldine base is blue and pernigraniline base is violet. The corresponding protonated forms are leucoemeraldine salt (colorless), emeraldine salt (green) and pernigraniline salt (blue but in a different shade than that of emeraldine base).

The oxidation of aniline in acidic aqueous media using ammonium peroxydisulfate as oxidant has become the most widely synthetic route to produce conducting PANI [3], which is obtained in the form of protonated emeraldine salt, named after its green colour. Emeraldine salt is the one that shows greater electrical conductivity than the rest of states and is highly stable in environmental conditions (presence of air, humidity).

Metal particles (e.g. Au, Ag, Pt, Pd) can be readily deposited on

these polymers by direct chemical or electrochemical redox reactions between the polymer and the oxidative metal cations [4,5]. However, it is not easy to control the size and distribution of the metal particles across the polymer matrix. Many catalyzed reactions require small monodispersed metal particles to achieve a high catalytic activity, so reduction of metal precursors is necessary. The catalytic properties of metal species are closely related to their morphology and particle size, which are normally determined by the reduction conditions. In many cases, catalysts are reduced by flowing hydrogen at elevated temperatures or by chemical reductants, such as formaldehyde, hydrazine or sodium borohydride. Non-thermal Ar plasma has been proposed as an alternative reduction technology operating at room temperature, which complies with the requirements of green chemistry, and is easy to perform [6–8]. The reducibility of metal ions by plasma can be determined by the value of their standard electrode potential; thus, those metal ions with positive standard electrode potential, such as Pd, Pt, Au, Ag, Rh and Ir can easily be reduced by non-hydrogen plasma at room temperature. It is well known that these metals have very interesting applications in catalysis [9].

In this research work, polypyrrole and polyaniline have been synthesized by chemical polymerization with sodium peroxydisulfate as oxidant. These polymers have been used as support for platinum catalysts, using H_2PtCl_6 as the metal precursor and Ar plasma to reduce it to metallic platinum. The synthesis and characterization of the polymer-supported catalysts, and their catalytic performance in the reduction of nitrates in water have been discussed. Nitrates are found in excess in water due to the use of fertilizers and waste effluents from industry. Nitrate pollution can cause water reservoirs eutrophication and it is also harmful for humans as it produces cancer and the commonly known blue-baby disease. The European legislation [10] has established a maximum permitted level of nitrate, nitrite and ammonium in water of 50, 0.5 and 0.5 mg L^{-1} , respectively. Recommendations by the World Health Organization (WHO) [11] are similar. Catalytic nitrate reduction at room temperature is a promising process, based on the use of bimetallic catalysts, generally associating a noble metal to a reducible promotor (Cu, Fe, Sn, In etc.) on a classical support, or of monometallic catalysts where the noble metal is deposited on a reducible support [12]. In many cases, the efficiency of the studied catalysts is not satisfactory as high concentrations of toxic nitrite or ammonium by-products instead of the desired nitrogen are produced. In this sense, it is of great interest to develop catalytic systems that are active in the reduction of nitrates in water, with a high selectivity to nitrogen instead of nitrites or ammonia. Metal catalysts supported on conductive polymers have demonstrated promising performances in this sense [13].

2. Experimental

2.1. Materials preparation

Polypyrrole (PPy) and polyaniline (PANI) were synthesized by chemical polymerization, using potassium peroxydisulfate ($\text{K}_2\text{S}_2\text{O}_8$) as oxidant (Schemes 1 and 2). In this study, the oxidant/pyrrole molar ratio was 2.33 and the oxidant/aniline molar ratio was 1.25 [13].

PPy was synthesized as follows: 9 g of oxidant ($\text{K}_2\text{S}_2\text{O}_8$) were dissolved in 200 mL of ultrapure water. Then, 1 mL of pyrrole ($\text{C}_4\text{H}_5\text{N}$, $M_m = 67.09 \text{ g mol}^{-1}$) was added drop wise, and the solution was stirred for 6 h at room temperature. As soon as the pyrrole is mixed with the oxidant solution, it turned to its characteristic black color, indicating the formation of oxidized PPy. The precipitated polypyrrole powder was filtered, washed with distilled water and dried at 80 °C for 12 h.

For the synthesis of PANI, 3.7 g of $\text{K}_2\text{S}_2\text{O}_8$ were dissolved in 75 mL of HCl (0.2 mol L^{-1}), 1 mL of aniline ($\text{C}_6\text{H}_5\text{NH}_2$, $M_m = 93.13 \text{ g mol}^{-1}$) was added drop wise and the solution was stirred for 12 h at room temperature. As soon as the aniline mixed with the oxidant solution, it turned to dark green color, characteristic of the emeraldine salt form of PANI. The precipitated polyaniline powder was filtered, washed with a solution of HCl (0.2 mol L^{-1}) until yellowish washing waters turned uncolored, and dried at 80 °C for 12 h.

The monometallic catalysts supported on polypyrrole and on polyaniline were prepared by impregnating the polymers with an aqueous solution of H_2PtCl_6 , used as the metal precursor. The proper amount of this salt to obtain 2 wt.% Pt loading was dissolved in ultrapure water, and then PPy or PANI were added to the solution (25 mL solution $\text{g}_{\text{polymer}}^{-1}$). The suspension was stirred for 12 h at room temperature, and then the solvent was removed by evaporation under reduced pressure in a rotary evaporator. The polymer-supported catalyst precursor was dried in an oven at 80 °C for 12 h and then was Ar plasma-treated in order to produce the metal catalyst.

The plasma treatment proceeded as follows [14]: The precursors of the polymer-supported catalysts were loaded on an aluminum boat, which was placed in the glow discharge stainless steel cylindrical chamber of a Tucano plasma system (Gambetti Kenologia, Italy), provided with an anodized aluminum door. The high frequency (HF) electrode is made of aluminum and has a “Dark Shield”, a radio

frequency (RF) 13.56 MHz power supply and mass flow controllers (MFC) for gas inlet control. The reaction chamber was evacuated to mild vacuum (0.15 Torr) using a Pfeiffer rotary vane pump (model PK D41 029C-Duo 2.5 with F4 Fomblin lubricant YL VAC 25/6). Ar (99.9999% minimum purity, Air Liquid) was introduced into the plasma chamber over the specimen (pressure of 0.5 mbar). Care was taken to pump down and purge the plasma reactor for at least 10 min prior to activating the RF field. The discharge power was set to 200 W and 36 cycles of 5 min each were applied to each sample (180 min treatment in total) with manual mixing of the sample between treatments to assure an even exposure to the plasma. The temperature of the sample after the plasma treatment was measured by a non-contact infrared thermometer (PCE Instruments, model PCE-888). It could be determined that the surface temperature was below 50 °C in all cases.

2.2. Materials characterization

The electrical conductivity of the prepared materials was calculated from resistance measurements, which were carried out in a home-made four-points probe equipment consisting in a cylindrical Teflon sample holder connected to a 2000 Multimeter (Madrid, Spain) through copper electrodes.

The textural characterization of the polymers was carried out by N_2 adsorption at -196°C with a Coulter Omnisorp 100CX equipment. Samples were previously outgassed at 150 °C for 4 h.

ATR-IR spectra were recorded on a Tensor 27 spectrophotometer (Bruker Optics, Billerica, MA USA) in the 600–4000 cm^{-1} range, using a zinc selenide crystal. 200 scans and a resolution of 4 cm^{-1} were used.

X-ray photoelectron spectroscopy (XPS) analysis was used to obtain information on the surface chemical properties. A K-Alpha spectrometer (Thermo-Scientific) with an Al K_α achromatic X-ray source (1486.6 eV) operating at 50 keV pass energy and 300 W was used. The pressure inside the analysis chamber was held below $5 \cdot 10^{-9}$ mbar during the course of the analysis. The measurements were carried out using a take-off angle of 45°. Survey scans were taken in the range 0–1350 eV, and high resolution scans were obtained on all significant peaks in the survey spectra. The intensities were estimated by calculating the integral of each peak, after subtraction of the S-shaped background, and by fitting the experimental curve to a combination of Lorentzian (30%) and Gaussian (70%) lines. Binding energies (B.E.) were referenced to the C 1 s photopeak position for C–C and C–H species at 284.6 eV, which provided binding energy values with an accuracy of ± 0.2 eV.

X-Ray diffraction (XRD) patterns of polymers were obtained with a D8-Advance (Bruker) X-ray diffractometer equipped with Göebel mirror and a Cu anode which provides K_α radiation ($\lambda = 1.5406 \text{ \AA}$). The samples were scanned from $2\theta = 6^\circ$ to 90° at the step scan mode (step size 1° , step time 3 s).

Transmission electron microscopy (TEM) images were taken with a JEM-2010 (JEOL Ltd., Tokyo, Japan) equipment operating at 120 kV. The sample material was mounted on a holey carbon film supported on a Cu grid by drying a droplet of an aqueous suspension of ground sample on the grid. EDX coupled to the TEM microscope provided elemental analysis of the samples.

2.3. Catalytic behavior

The catalytic behavior of the polymer-supported catalysts was evaluated in the reduction of aqueous nitrate under H_2 at room temperature. A semi-batch reactor equipped with a magnetic stirrer (700 rpm) was fed with 592.5 mL of deionized water and 300 mg of catalyst. The reduction of nitrate leads to the formation of hydroxide ions, which cause the increase of pH value up to 10 [15]. To avoid it, the system was buffered with a CO_2 flow to keep a constant value of $\text{pH} \approx 5$. During the reaction tests, H_2 and CO_2 were passed for 15 min through the reactor at respecting flow rates of $75 \text{ cm}^3 \text{ min}^{-1}$ to assure removal of oxygen. Afterwards, 7.5 mL of an aqueous NaNO_3 solution

was added; in this way, the initial concentration of NO_3^- in the reactor was 100 mg L^{-1} . Aliquots (1 mL) were withdrawn at different times from the reactor, and immediately filtered for determination of nitrate, nitrite and ammonium ions concentrations by ion chromatography, using a Metrohm 850 ProFlC AnCat-MCS equipment, with a Metrosep ASSUPP-7 column ($250 \text{ mm} \times 4 \text{ mm}$) for nitrate and nitrite anions determination, and a Metrosep C3 column ($250 \text{ mm} \times 4 \text{ mm}$) for ammonium cation determination.

Nitrate conversion ($X_{\text{NO}_3^-}$, in%) was calculated as:

$$X_{\text{NO}_3^-} = \frac{[\text{NO}_3^-]_0 - [\text{NO}_3^-]_t}{[\text{NO}_3^-]_0} \cdot 100$$

where $[\text{NO}_3^-]_0$ is the initial nitrate concentration (mg L^{-1}) and $[\text{NO}_3^-]_t$ is the nitrate concentration (mg L^{-1}) at time t (min).

Selectivities (S , in%) to nitrite and ammonium were calculated as:

$$S_{\text{NO}_2^-} = \frac{(n_{\text{NO}_2^-})_t}{(n_{\text{NO}_3^-})_0 - (n_{\text{NO}_3^-})_t} \cdot 100 \quad \text{and} \quad S_{\text{NH}_4^+} = \frac{(n_{\text{NH}_4^+})_t}{(n_{\text{NO}_3^-})_0 - (n_{\text{NO}_3^-})_t} \cdot 100$$

where $(n_{\text{NO}_3^-})_0$ is the initial amount of nitrate (mol) and $(n_{\text{NO}_2^-})_t$, $(n_{\text{NO}_3^-})_t$, $(n_{\text{NH}_4^+})_t$ are the amounts of the respective species (mol) at time t (min).

The absence of metal leaching was checked by analyzing aliquots withdrawn from the reactor once the nitrate reduction reaction was completed, by Inducted Coupled Plasma Mass Spectrometry (ICP-MS). A 7700 x equipment (Agilent) was used: RF power 1150 W , He flow of 0.99 L min^{-1} and liquid flow of 0.3 mL min^{-1} .

3. Results and discussion

Polypyrrole and polyaniline chemically synthesized with $\text{K}_2\text{S}_2\text{O}_8$ showed electrical conductivities of 25 and 478 S m^{-1} and BET surface areas of 11 and $40 \text{ m}^2 \text{ g}^{-1}$, respectively. The pristine polymers and the catalysts have been fully characterized.

3.1. Characterization by FTIR

As-synthesized polypyrrole shows IR absorption bands characteristic of C=N–C species: C–N stretching at 1197 cm^{-1} , C=N stretching at 1562 cm^{-1} and C=N–C bending at 920 cm^{-1} (Fig. 1a, Table S.1.). The band at 1095 cm^{-1} corresponds [16] to the in-plane deformation vibration of NH^+ present in PPy after protonation (Scheme 1). Besides, the band at 1714 cm^{-1} (C=O stretching) is due to surface oxygenated groups created as a consequence of the reaction of the polymeric chain with water within the polymer network, as polypyrrole is hygroscopic. Spectrum of polypyrrole impregnated with H_2PtCl_6 (PPy/Pt) (Fig. 1c) shows asymmetric and symmetric stretching bands of C–H at 2920 and 2854 cm^{-1} , which indicates the existence of alkyl groups which may be

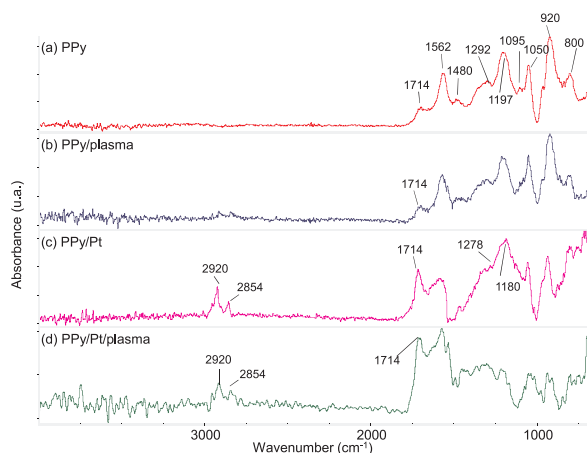


Fig. 1. FTIR spectra of PPy after different treatments.

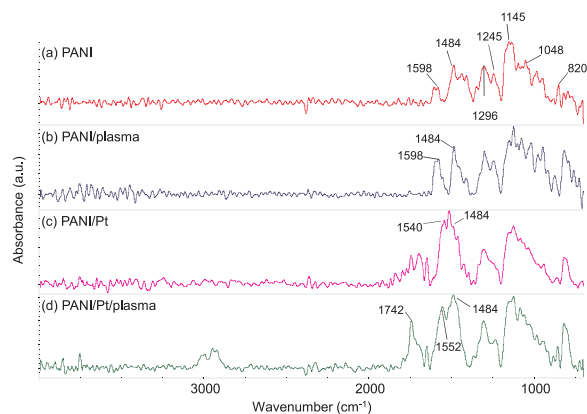


Fig. 2. FTIR spectra of PANI after different treatments.

originated by the breaking of some pyrrole rings [17]. Bands of C=N–C species are modified in shape when compared to pristine PPy in Fig. 1a, due to the interaction of platinum with nitrogen of the polypyrrole chain [14]. Besides there is an increase of the intensity of the C=O stretching band (1714 cm^{-1}) due to the degradation of the PPy surface by the aqueous H_2PtCl_6 solution, which creates more surface oxygen functionalities of the carbonyl type.

On the other hand, the spectra of polyaniline doped with $\text{K}_2\text{S}_2\text{O}_8$ shows typical bands of the polymeric chain [18,19] (Fig. 2a Table S.1). The absorption bands at 1598 and 1484 cm^{-1} correspond to the absorption of quinoid (Q) and benzenoid (B) ring-stretching deformations, respectively, characteristic of emeraldine [1,20]. The absorption band at 1296 cm^{-1} corresponds to π -electron delocalization induced in the polymer by protonation and the absorption band at 1245 cm^{-1} is characteristic [16] of the conducting protonated form and it has been ascribed to the C–N⁺ stretching vibration in the polaron structure (Scheme 2). The intense band at 1145 cm^{-1} has been ascribed [16] to a vibration mode of the $-\text{NH}^+$ = structure formed during protonation (Scheme 2). Impregnation of PANI with H_2PtCl_6 (PANI/Pt) (Fig. 2c) results in the presence of several bands between 1600 and 1800 cm^{-1} similar to overtones in benzene derivatives due to ring substitution. This suggests that conjugation in the polymeric chain is affected by the interaction of the platinum ion with nitrogen atoms. There is also a shift to lower wavenumbers of the quinoid band (1598 cm^{-1} in PANI to 1540 cm^{-1} in PANI/Pt), similar to those reported in the literature [18,21]. However, contrary to what was observed with PPy, bands corresponding to C–H stretching at 2920 and 2854 cm^{-1} are not evidenced in PANI.

The plasma treatment does not produce significant modifications in the IR spectra of PPy (Fig. 1b) and PANI (Fig. 2b), but it does affect the platinum-impregnated polymers. The spectrum of the plasma-treated impregnated polypyrrole (PPy/Pt/Plasma) (Fig. 1d) shows a decrease of the intensity of bands assigned to asymmetric and symmetric stretching of carbon-hydrogen bonds (C–H sy st and C–H as st) at 2920 and 2854 cm^{-1} , and an increase of the C=O stretching band (1714 cm^{-1}). Plasma treatment also creates oxygenated moieties on platinum-impregnated polyaniline (PANI/Pt/Plasma) (C=O stretching band at 1742 cm^{-1}). These C=O moieties are created when the plasma-activated polymer surface is put in contact with air (Fig. 2d).

3.2. XPS characterization

XPS surface analysis is useful to determine the degree of oxidation of the polymeric chains and the oxidation state of platinum species. Surface analysis of both polymers show carbon and nitrogen species from the polymeric chain, and also sulfur from the oxidant (Table S.2). Potassium peroxydisulfate may incorporate into the oxidized polymeric chains as a counter-ion, acting as a dopant, but it also might be

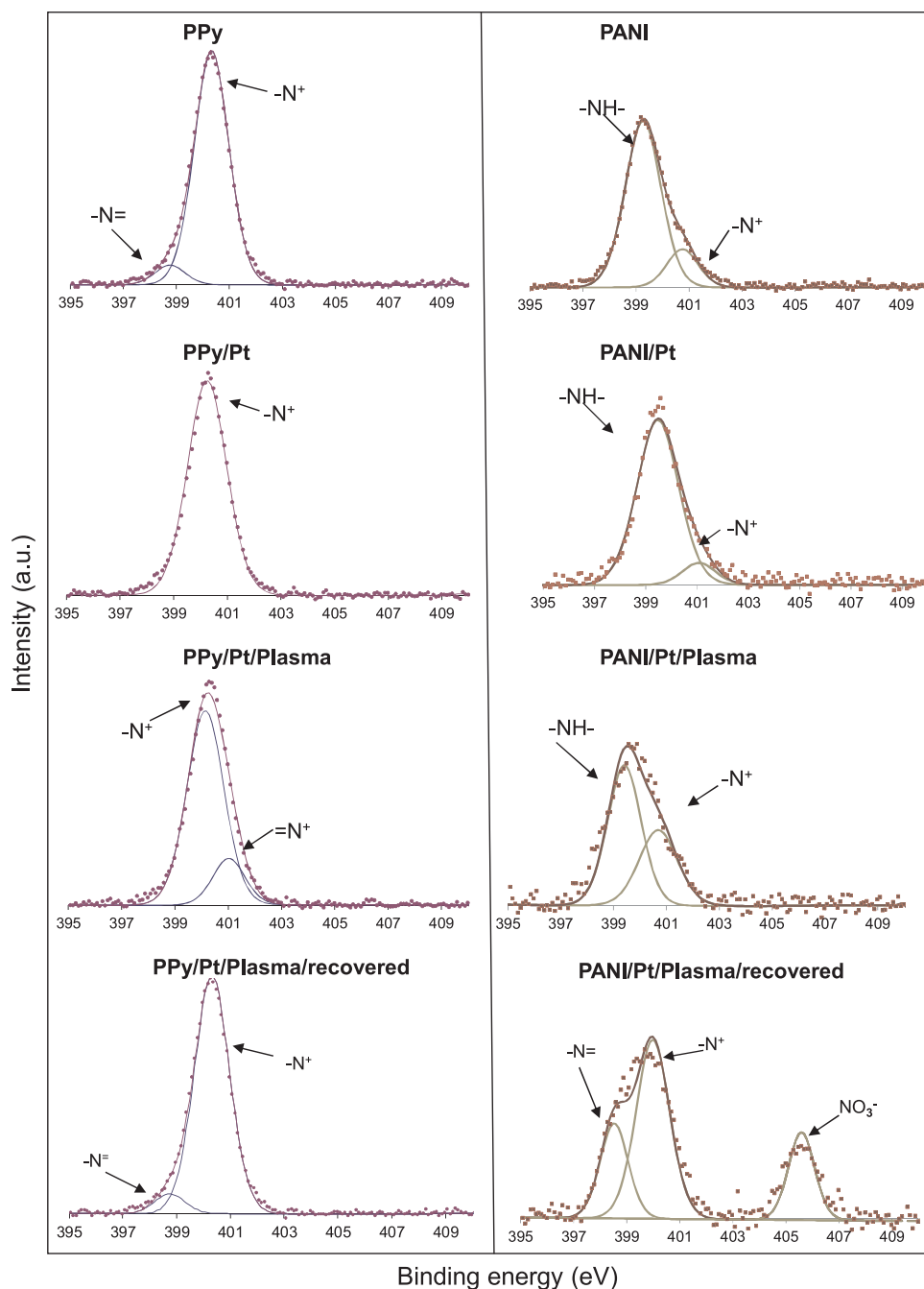


Fig. 3. XPS N 1s spectra of PPy and PANI and supported catalysts.

introduced as sulfate as a result of the redox reaction with the pyrrole or aniline monomers. The binding energy of the S 2p level peak, 168.3 eV, corresponds to SO_4^{2-} , what evidences the reduction of $\text{S}_2\text{O}_8^{2-}$ upon anchoring to the polymers. The presence of chlorine as chloride (there is a doublet corresponding to Cl 2p_{1/2} at 198.6 eV and Cl 2p_{3/2} at 197.1 eV) reveals the ability of Cl^- (from HCl in PANI synthesis) to produce the doping of the polymer in competition with SO_4^{2-} from peroxydisulfate. There is also a contribution of chlorine at a higher binding energy (Cl 2p_{1/2} at 201.9 eV and Cl 2p_{3/2} at 200.2 eV), which has been ascribed [18,22,23] to chlorine atoms covalently bound to aromatic rings in PPy and PANI. Analysis of the XPS spectra of the C 1s level (Table S.3) shows oxygenated moieties (C=O on the pristine PPy and C–O on pristine PANI), produced as a result of the contact of the polymer surface with water present in the reaction medium. This is consistent with FTIR data (Figs. 1 and 2). On the other hand, the oxidation degree of the polymeric chain, evaluated from the N 1s curve fit

Fig. 3, Table S.4), is different for both polymers. Thus, the pristine polypyrrole (PPy) chain shows a considerable higher percentage of oxidized nitrogen ($-\text{N}^+$) (93%) than the pristine polyaniline (PANI) (17%).

H_2PtCl_6 is a strong acid and anions formed during its dissociation are hydrolyzed in aqueous medium [24] to give a variety of chloro-aqua complexes such as $[\text{PtCl}_6]^{2-}$, $[\text{PtCl}_5(\text{H}_2\text{O})]^-$, and $[\text{PtCl}_3(\text{H}_2\text{O})]^-$. These complexes may anchor to nitrogen species of the polymeric chain [18,23,25]. XPS analysis detects platinum on the polymers surfaces. Analysis of the Pt 4f level in polypyrrole and polyaniline impregnated with H_2PtCl_6 (Fig. 4) shows two predominant bands at 72.9 eV (Pt 4f_{7/2}) and 76.3 eV (Pt 4f_{5/2}), which correspond to Pt^{2+} , and represent 86% (in PPy) and 91% (in PANI) (Table S.5). Pt^{4+} is also detected in both polymers (bands at 74.0 eV (Pt 4f_{7/2}) and 77.4 eV (Pt 4f_{5/2})). This suggests that Pt^{4+} suffers spontaneous reduction to Pt^{2+} by electrons provided by the polymeric chain. The absence of metallic platinum is

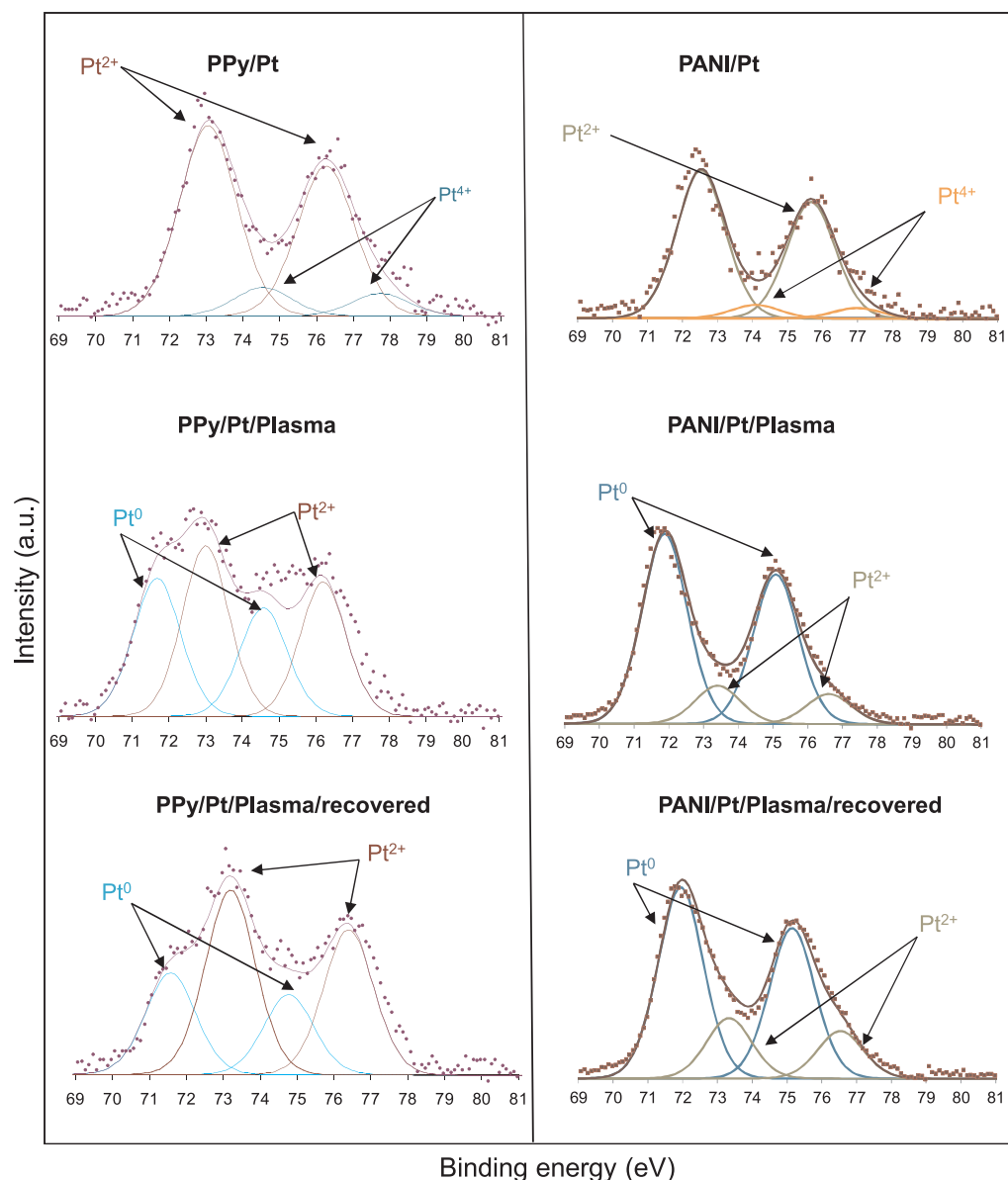
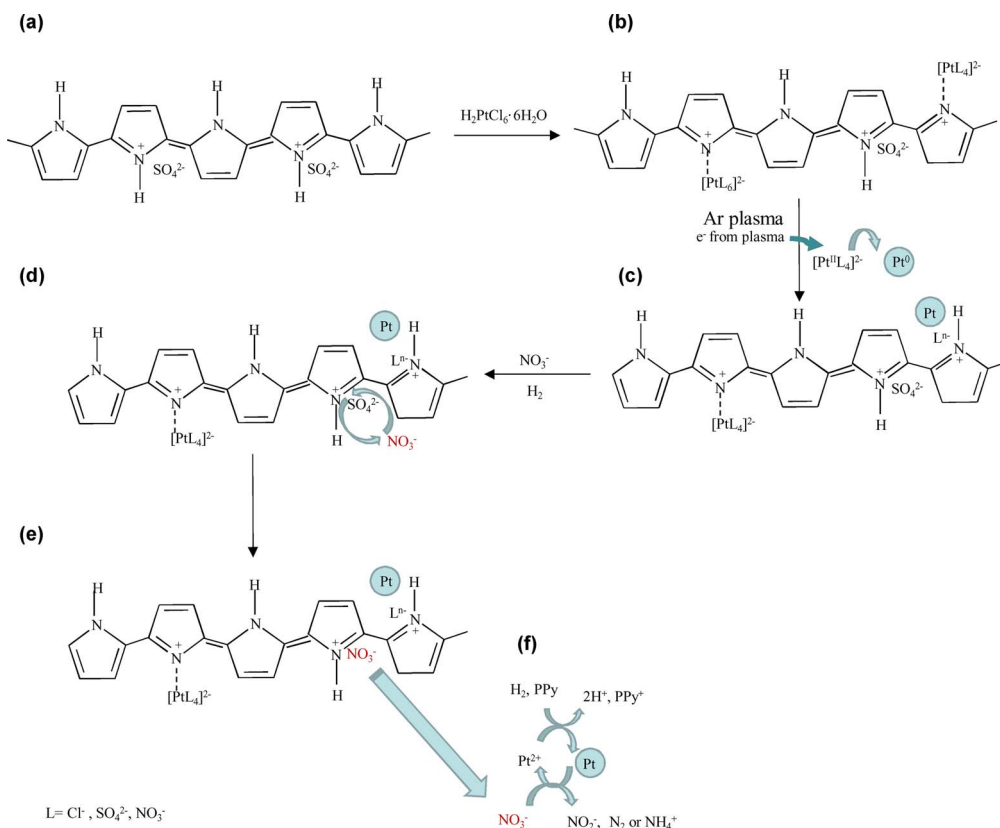


Fig. 4. XPS Pt 4f spectra of PPy and PANI and supported catalysts.

confirmed by the absence of bands that should appear at lower binding energies, typically at 71.1 eV (Pt 4f_{7/2}) and 74.4 eV (Pt 4f_{5/2}). Redox potentials shown in Table S.6 confirm that the reduction of [PtCl₆]²⁻ to [PtCl₄]²⁻ during the impregnation process is possible, and it should be accompanied by oxidation of the polymeric chain. The oxidation of the PPy chain upon impregnation with hexachloroplatinic acid is evidenced by the disappearance of the reduced imine moieties (=N- at 397.9 eV) shown in pristine PPy, which are not present in the platinum-impregnated PPy, where only oxidized amine groups are depicted (-N⁺- at 400.5 eV) (Fig. 3, Table S.4). It can be assumed that Pt(IV) species from H₂PtCl₆ are initially introduced as [PtCl₆]²⁻ counter-ions of PPy and PANI (synthesized as the conductive emeraldine salt form), but they are easily reduced to Pt(II) species which coordinatively bond to the polymeric chain as a platinum chloro complex. Sulfate ions from the dopant (K₂S₂O₈) used in the synthesis of both PPy and PANI, and also chlorine coming from the acid medium (HCl) used in the synthesis of PANI, could act as counter-ions of the oxidized nitrogen moieties (N⁺) of the polymeric chain, as well as ligands of the platinum complex (Scheme 3b). The reductive ability of the polymers is responsible for the observed reduction of Pt(IV) to Pt(II) in this platinum complex, but no metallic platinum is observed.

XPS analysis shows that treatment with non-thermal argon plasma is able to partially reduce platinum ions into Pt(II) and metallic platinum in the polymer-supported catalyst. Consequently, Pt(IV) is not further present on any polymer after treatment in argon plasma. However, the effectiveness of reduction treatment with Ar plasma depends on the polymer nature. This was already demonstrated for Pt deposited onto PPy [14,26]. The reduction mechanism produced by plasma treatment is quite different from widely used redox processes involving reductive chemicals as sodium borohydride. This one is an inner sphere mechanism of re-emplacment of chlorine and/or sulfate ligands by BH₄⁻, followed by a redox reaction where electron transfer in the intermediate complex is produced [27]. Otherwise, when a cold plasma treatment is performed, the energetic electrons present in the plasma serve as reducing agents for the platinum ions (Scheme 3b,c). In the case of PANI support, platinum ions anchored to N⁺ moieties located out of the aromatic ring in PANI (Scheme 4b) are more easily reduced than platinum ions anchored to N⁺ located inside the ring in PPy (Scheme 3c). Therefore, considerably higher amount of metallic platinum is detected on PANI surface (83%) compared to PPy (47%) after plasma treatment (Table S.5). Formation of platinum nanoparticles implies dissociation of the platinum complexes anchored to the



Scheme 3. Proposed mechanisms for nitrate abatement from water in the presence of platinum nanoparticles supported on PPy.

polymeric chain through the nitrogen functionality ($-\text{N}^+ - [\text{PtL}_4]^{2-}$) (Scheme 4b). As a result, there is a change in the oxidation state of the polymeric chain, which becomes oxidized, as assessed by N 1s contributions: 62% of amine $-\text{NH}-$ groups and 38% of oxidized amine N^+ groups are detected in the plasma treated PANI. PPy oxidation is even more important with the presence of 83% of $-\text{N}^+$ (at 400.5 eV) and 17% of $\text{N}^+ =$ moieties (at 401.0 eV). The ligands released from the dissociated platinum complex (L^n) (Scheme 3c) could act as counteranions to stabilize the oxidized polymeric chain.

3.3. XRD characterization

PPy and PANI X-ray diffraction patterns (Fig. 5) are characteristic of amorphous polymers, showing three broad bands. One band centered at $2\theta = 17-18^\circ$ for PPy and $2\theta = 18-20^\circ$ for PANI corresponds to the periodicity along the polymeric chain, another band centered at $2\theta = 25^\circ$ for PPy and $2\theta = 27-28^\circ$ for PANI corresponds to the periodicity perpendicular to the polymer chain [18]. The third band at

$2\theta = 42^\circ$ in both polymers is also typical of the polymer phase [19].

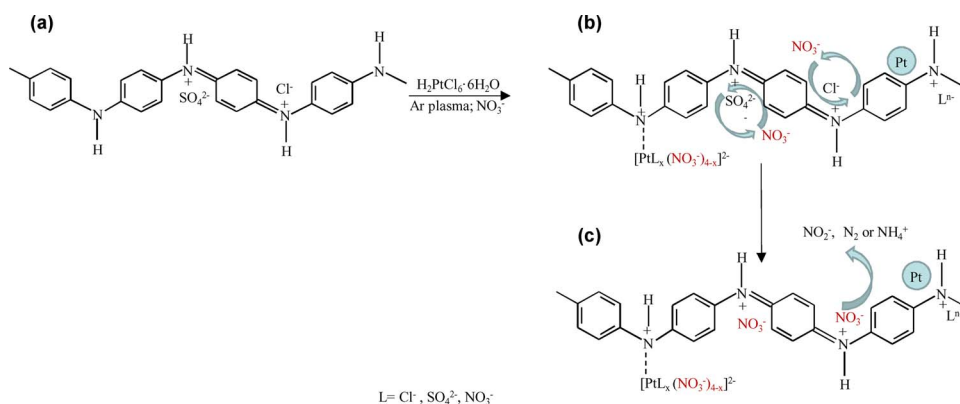
X-ray diffraction patterns of polymers impregnated with Pt and treated with Ar plasma do not show reflexions due to crystalline metallic platinum, which should be located at $2\theta = 39.8^\circ$ for Pt(100) and 46.2° for Pt(200) [18,28], indicating a high metallic dispersion.

3.4. Characterization by TEM

TEM micrographs (Fig. 6a) show the PPy and PANI polymeric supports alone and after deposition of Pt before and after plasma treatment. After deposition of platinum on the supports, platinum nanoparticles are only visible after treatment with Ar plasma. The average size of the nanoparticles is 4.5 nm when supported on PPy and 5.0 nm when supported on PANI (Fig. 6b).

3.5. Catalytic behavior

The redox mechanism of nitrates removal involves a first step in



Scheme 4. Proposed mechanisms for nitrate abatement from water in the presence of platinum nanoparticles supported on PANI.

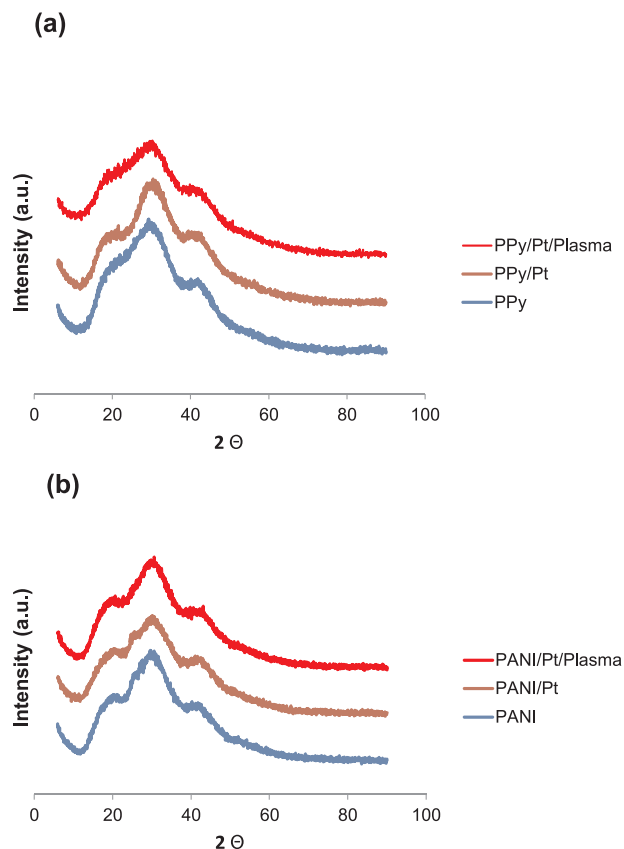


Fig. 5. XRD patterns of (a) PPy and (b) PANI and supported catalysts.

which nitrates are reduced to nitrites, followed by the reduction of nitrites to N_2 and/or ammonium [13,15,29–31]. Table S.6 shows the redox potentials of nitrate reduction to the desired N_2 and to the undesired ammonium. Although this reaction is thermodynamically favored, a catalyst is needed for the reaction to proceed at a measurable rate. A blank experiment, which consisted on flowing the reducing agent (H_2) and the buffer (CO_2) through the aqueous nitrate solution in the absence of any catalyst, and analyzing by ion chromatography

Table 1

Nitrate, nitrite and ammonium concentrations, nitrate conversion and selectivities to nitrite and ammonium after 5 min of reaction.

Sample	(mg L ⁻¹)			(%)		
	[NO ₃ ⁻]	[NO ₂ ⁻]	[NH ₄ ⁺]	X _{NO₃⁻}	S _{NO₂⁻}	S _{NH₄⁺}
PPy/Pt/Plasma 1st cycle	48.65	0.04	2.25	51	0.10	15
PANI/Pt/Plasma 1st cycle	42.42	0.01	0.13	57	0.02	0.8
PPy/Pt/Plasma 2nd cycle	50.01	0.03	2.00	50	0.08	13
PANI/Pt/Plasma 2nd cycle	46.36	0.01	0.10	53	0.05	0.6

aliquots periodically extracted from the solution, revealed that nitrate concentration was unaltered after 300 min and that neither nitrite nor ammonium were detected. Therefore, in this work, the catalytic activity of platinum nanoparticles synthesized by argon plasma treatment onto polypyrrole and polyaniline has been tested in the catalytic reduction of nitrates in water with hydrogen.

A decrease of nitrate concentration below 50 mg L⁻¹ is produced within the first 5 min of reaction with the platinum catalysts supported on both polymers, with 51 and 57% conversion achieved with PPy and PANI, respectively (Table 1). These measured concentrations remained constant with time up to 300 min (Fig. S.1.). Besides, selectivity of the reaction to nitrite is extremely low, in such a way that measured nitrite concentrations are much smaller than the maximum permitted levels of nitrite in drinking water (0.5 mg L⁻¹) [10,11]. Although a very low ammonium concentration is detected when the platinum catalyst is supported on PANI (0.13 mg L⁻¹) (Table 1), contrary to what is observed when platinum is supported on PPy, (2.25 mg L⁻¹), this amount exceeding the maximum allowed ammonium concentration (0.5 mg L⁻¹). It is not possible to measure nitrogen production, but the ammonium concentration detected in the reactor reveals that a redox process is taking place. These data suggest that the removal of nitrate on the polymer-supported Pt catalysts is not a simple adsorption process that may occur at the catalyst surface. Nitrate anions can be exchanged with the dopant counter-ions [32], but they can also be retained by interaction with the chloro-platinum complex [33]. Thus, it has to be considered that dopant anions are inserted in the polymer matrix, bigger dopants occupying a larger space. Taking into account the relative ionic radius of dopants (258 pm for sulfate anion, 181 pm for chloride anion) and nitrate anion (179 pm for NO₃⁻), ion exchange

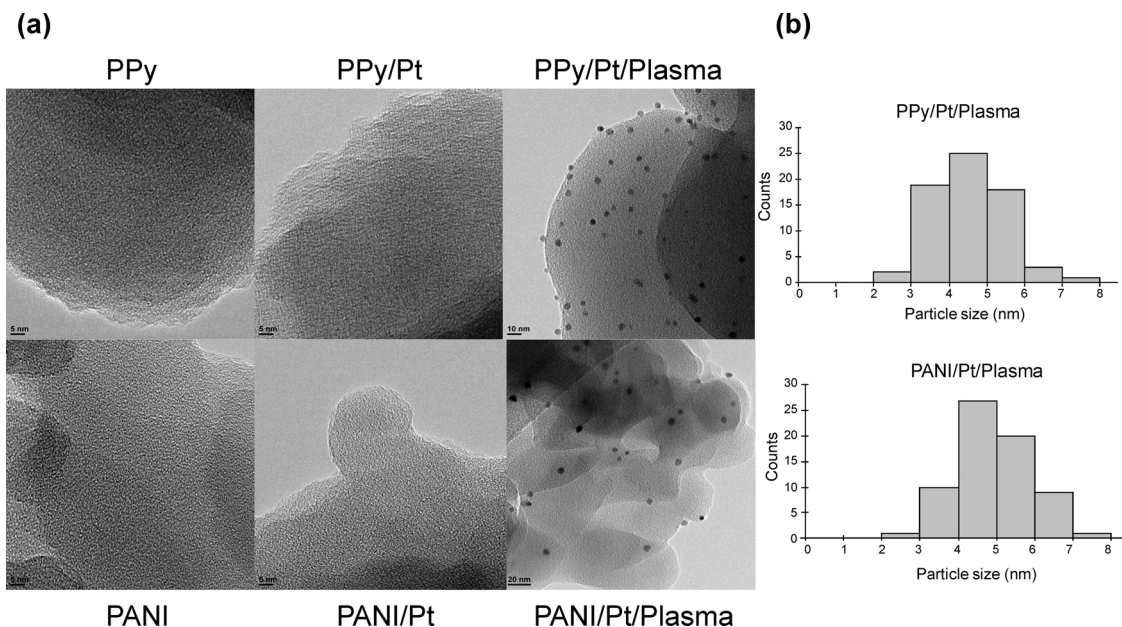


Fig. 6. (a) TEM micrographs and (b) particle size distributions of PPy and PANI and supported catalysts.

between nitrate and counter-ions resulting from polymer doping (SO_4^{2-} in both PPy and PANI, and Cl^- from HCl in PANI) is possible. XPS characterization of the catalyst before and after reaction evidences the exchange between the dopants and nitrate (Table S.2), with considerable lower Cl and S concentrations and increased N amounts in the polyaniline-supported catalyst recovered from the reactor after being in contact with the nitrate aqueous solution, compared to the pristine polymer. Furthermore, the XPS spectra of the N 1s level of PANI/Pt/Plasma/recovered (Fig. 3) also shows an important contribution of nitrate (406.0 eV), which suggests that nitrate was retained by PANI. However, no nitrate contribution is observed in PPy/Pt/plasma/recovered. Considering that not all the platinum ions in the chloro-complexes have been reduced to the metallic state by the plasma treatment, and that a considerable amount of Pt(II) was still present, as assessed by XPS, nitrate could form an adduct with the platinum complex or even enter in its coordination sphere as a ligand ($[\text{PtL}_x(\text{NO}_3^-)_{4-x}]^{2-}$) (Scheme 4b). The minimized steric hindrance provided by the location of the nitrogen atom external to the ring in PANI, compared to PPy, favors the removal of nitrate from water by this mechanism in the presence of PANI, which could explain the lower formation of ammonium ions on PANI/Pt/Plasma compared to its PPy counterpart (Table 1). If a large amount of nitrate just remained anchored to the polymeric chain as NO_3^- by ion exchange, with no further reduction, further treatment or disposal of nitrate containing polymers would be necessary, which is also an environmental concern. It is not possible to measure N_2 production, but there is some ammonium production (Table 1), which suggests that at least some of the nitrate initially retained by PANI is reduced by a catalytic way. In this case, nitrate is firstly exchanged with SO_4^{2-} and Cl^- counter-anions present in doped PANI (Scheme 4b) and, in a second step, it suffers reduction by the electrons provided by the polymeric chain through the nitrogen functionality (Scheme 4c).

In polypyrrole (Scheme 3a), the nitrogen atom located within the aromatic ring minimizes the possibility of formation of an adduct or enter as a ligand into the platinum complex. Thus in polypyrrole, ion exchange between counter-ions present in the doped polymer and NO_3^- from the nitrate aqueous solution is produced in a first step (Scheme 3d), followed by reduction of nitrate by electrons from the polymer (Scheme 3f). As a result, no nitrate is retained, as evidenced by XPS.

Recyclability of the catalysts was tested. Thus, the catalysts recovered after one reaction cycle were put into contact with a 1 M solution of NaCl during 30 min under stirring with the purpose of regenerate them by exchanging adsorbed nitrate anions with chloride ions. Both catalysts, irrespective of their ability in adsorbing nitrate during the course of the reaction were treated in the same way, for comparison purposes. Table 1 shows that the nitrate conversions achieved with both regenerated catalysts are only slightly lower than those obtained during the first run. Similar ammonium selectivities were obtained and nitrite was not detected in any case.

The inherent ability of conducting polymers such as PPy and PANI of switching between different oxidation states imparts them the capability of acting as a source and or a drain of electrons, depending on the redox process in which they are involved [33,34]. Upon reduction of nitrate, some of the metallic platinum is oxidized to Pt^{2+} (Fig. 4, Table S.5), what is accompanied by a reduction of the oxidation state of the polymeric nitrogen, as evidenced in the recovered polymers (Fig. 3, Table S.5). Evidence of donation of electron density from platinum nanoparticles to polypyrrole has been previously reported [35]. These results show that the polymeric matrix participates in the redox process by switching between different oxidation states as a response to the electron transfer from platinum to nitrate (Scheme 3f).

The hydrogen flow into the reactor avoids any contact with air of the plasma-reduced Pt catalyst before and during the course of the reaction [29], and it could also contribute to the regeneration of oxidized Pt^{2+} to Pt^0 . Lixivated platinum measured by ICP-MS was always less

than 0.05% (Table S.7).

On both catalysts, both platinum ions in form of a platinum complex and metallic platinum nanoparticles are detected by XPS. The presence of platinum in both oxidation states significantly alters the redox properties of the polymers. Metallic platinum may promote reduction of nitrate [33,36] and oxidized platinum species may promote oxidation of the polymer. Therefore, continuous electron transfer between the polymer and nitrate is being produced.

4. Conclusions

Platinum nanoparticles have been synthesized on polyaniline and polypyrrole from a platinum salt precursor using a reducing treatment with cold Ar plasma. These catalysts produce an important abatement of nitrate from water in only 5 min. However, nitrate abatement proceeds by two different mechanisms, depending on the nature of the conducting polymer:

Mechanism A: Nitrate is adsorbed on the platinum complex either forming an adduct or entering the complex as a ligand. This mechanism is favored in PANI, where the nitrogen atom is external to the ring system and steric hindering is minimized.

Mechanism B: There is an ion exchange between Cl^- and/or SO_4^{2-} present in the doped polymers as counter-ions and NO_3^- from the nitrate aqueous solution. This mechanism is favored in PPy.

In both cases, the adsorption or ion exchange of nitrate is followed by a redox process in which metallic platinum nanoparticles synthesized by argon plasma have a role in the reduction of nitrate to either ammonium (measured) and nitrogen (not measured). Ammonium production was more important when platinum was supported on PPy compared to PANI, but it was maintained constant with reaction time. The location of the nitrogen atom within the aromatic ring in PPy restricts the extension of mechanism A, and favors mechanism B, which involves the reduction of nitrate located next to platinum nanoparticles.

As a result of any of the redox process involving platinum, that is, platinum ions being reduced by electrons coming from plasma and, on the other hand, metal platinum nanoparticles being oxidized as nitrate is reduced, the oxidation state of the polymeric chain changes. This evidence an active participation of the polymer matrix in the redox process.

Regeneration of the catalysts data showed that the removal of nitrate ability was maintained after two cycles.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.apcatb.2017.11.064>.

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